Application No. 10/643,974

Reply to Office Action of August 3, 2006

IN THE SPECIFICATION

Please replace the paragraph beginning at page 7, line 20, through page 8, line 14, with the following rewritten paragraph:

A fuel cell catalyst material according to the present invention is obtained by nitriding ultrafine platinum-based particles. When nitrogen is added to an element or compound, a new property is given to the element or compound to improve its original material performance. Since this phenomenon is often observed, research and development of nitrides such as AlN, GaN, and SmFeN are being extensively made. Pt can form various alloys and compounds with other elements. However, since Pt is extremely stable against nitrogen, only a bulk alloy nitride containing a small amount of Pt, such as Fe₃PtN, can be obtained. On the other hand, a nanosize material increases the ratio of atoms on the material surface, so the characteristics of the surface atoms have influence on the performance of the whole material. Accordingly, the characteristics of a material may be changed by downsizing the material to [[a]] nanosize. The present inventors have found that a highly active and highly stable fuel cell catalyst can be obtained by adding a nitrogen element to ultrafine platinum-based particles having a specific composition, and have completed the present invention.

Please replace the paragraph at page 8, lines 15-20, with the following rewritten paragraph:

The second invention embodiment is a fuel cell catalyst material manufacturing method comprising nitriding a catalyst precursor containing platinum-containing particles at a temperature of 200°C to 1,000°C for 0.05 to 100 hrs in a gas atmosphere containing NH₃ with a partial pressure of 0.05 atm or more.

Please replace the paragraph beginning at page 8, line 21, through page 9, line 1, with the following rewritten paragraph:

The present inventors made extensive studies, and have found that when a catalyst material containing platinum-containing particles is to be nitrided, the activity of N atoms is higher in an NH₃ atmosphere than in an N₂ atmosphere, so the platinum-containing particles can be nitrided by the combined effect of this highly active NH₃ atmosphere and downsizing of the platinum-containing particles to [[a]] nanosize.

Please replace the paragraph at page 9, lines 2-5, with the following rewritten paragraph:

The third invention embodiment is a fuel cell electrode having a catalyst layer in which a catalyst material containing fine ferromagnetic catalyst particles is arranged in one direction.

Please replace the paragraph beginning at page 10, line 14, through page 11, line 1, with the following rewritten paragraph:

Pt can improve the activity and chemical stability of the catalyst. If the atomic ratio of Pt is less than 1, the chemical stability of the catalyst material <u>is</u> significantly <u>lowers</u> lowered. Each of Ru, Pd, Au, and Ag has performance similar to those of Pt and hence can help improve the activity and chemical stability of the catalyst. However, if the content of these noble metal elements in the element A exceeds 60 at%, the activity or chemical stability of the catalyst material may <u>be lower lowered</u>. Therefore, the content of at least one noble metal element in the element A is preferably 60 at% or less, and more preferably, 50 at% or

less. Especially when the catalyst material is to be used as an anode catalyst material, the element A is desirably made up of 50 at% of Pt and 50 at% of Ru.

Please replace the paragraph at page 11, lines 6-22, with the following rewritten paragraph:

The element T can increase the activity of the catalyst, and can be nitrided more easily than Pt. When the element T is contained in the platinum-containing catalyst particles, nitriding of the catalyst particles can be promoted. When an atomic ratio \underline{x} is 0.2 or more, a satisfactory nitriding promoting effect can be obtained. However, if the atomic ratio \underline{x} of the element T exceeds 4, the chemical stability of the catalyst material $\underline{i}\underline{s}$ significantly lowers lowered. Also, when an element containing at least one of Fe, Co, and Ni is used as the element T, a ferromagnetic catalyst material can be obtained. In this case, the atomic ratio \underline{x} of the element T is preferably 0.25 (inclusive) to 4 (inclusive). In particular, Fe, Co, Mo, W, Cr, and Ag can well increase the catalyst activity of a noble metal such as Pt, and can promote nitriding.

Please replace the paragraph beginning at page 12, line 19, through page 13, line 10, with the following rewritten paragraph:

Although the average diameter of the catalyst particles represented by formula (1) presented earlier is not particularly limited, this average diameter can be set at 0.5 to 500 nm for the reasons explained below. If the average diameter is less than 0.5 nm, surface oxidation, flocculation, or sintering of the catalyst particles intensely occurs. Since this decreases the activation site density on the catalyst particle surface, the activity or stability of the catalyst material may be lower lowered. If the average diameter exceeds 500 nm, the specific surface area of the catalyst particle reduces is reduced. This lowers the activation

site density and makes it difficult to obtain high activity. Also, if nitriding is so performed as to make the average diameter larger than 500 nm, it becomes difficult to add nitrogen particularly to platinum rich particles. The average diameter is more preferably 0.5 to 50 nm, and most preferably, 1 to 10 nm.

Please replace the paragraph at page 14, lines 4-6, with the following rewritten paragraph:

The fuel cell catalyst material manufacturing method according to the second invention embodiment will be explained below.

Please replace the paragraph at page 17, lines 1-8, with the following rewritten paragraph:

An electrode composition containing the fuel cell catalyst material according to the first invention embodiment will be described below. This electrode composition contains a proton conductive material and the fuel cell catalyst material according to the present invention. A conductive substance such as graphite or a polymer such as PTFE may also be added, if the addition is effective for electrode formation.

Please replace the paragraph at page 20, lines 17-18, with the following rewritten paragraph:

The fuel cell electrode according to the third invention embodiment will be described below.

Please replace the paragraph at page 25, lines 4-20, with the following rewritten paragraph:

In the membrane-electrode assembly according to the present invention, when the catalyst material particles containing the ferromagnetic catalyst having the composition represented by formula (2) [[is]] are to be contained in an anode electrode, this anode electrode includes an anode catalyst layer containing the catalyst material, and a collector which carries this anode catalyst layer. At least one part of the catalyst material particles stack in the thickness direction of the anode catalyst layer. In addition, the content of the catalyst material on the surface of the anode catalyst layer that opposes the collector is made larger than that of the catalyst material on the surface which opposes an electrolyte layer. In this manner, the utilization of fuel (e.g., an aqueous methanol solution) in the anode catalyst layer can be increased.

Please replace the paragraph at page 26, lines 9-11, with the following rewritten paragraph:

A method of manufacturing the fuel cell electrode according to the third invention embodiment will be described below.

Please replace the paragraph at page 26, lines 18-23, with the following rewritten paragraph:

An apparatus for manufacturing the fuel cell electrode according to the third invention embodiment is used in the fuel cell electrode manufacturing method according to the present invention, and comprises a magnetic field generating unit which includes at least one of an electromagnet and a permanent magnet.

Please replace the paragraph at page 32, lines 11-22, with the following rewritten paragraph:

1 g of an anode catalyst material in which carbon particles earries carry PtRu alloy particles having an average diameter shown in Table 1 and 2 g of pure water were well stirred. In addition, 4.5 g of a 20% Nafion solution and 10 g of 2-ethoxyethanol were added, and the resultant solution was well stirred. After that, the material was dispersed by a bench ball mill to form a slurry. Water-repellent carbon paper (350 µm, manufactured by TORAY INDUSTRIES) was coated with the slurry by using a control coater, and the resultant material was air-dried to form an anode electrode having a catalyst carrying density of 2.5 mg/cm².

Please replace the paragraph at page 36, lines 21-26, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was formed and the cell performance [[were]] was evaluated following the same procedures as in Example 1, except that a cathode catalyst material formed by a method explained below was used. The results are shown in Table 1.

Please replace the paragraph beginning at page 39, line, 24 through page 40, line 2, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was formed and the cell performance [[were]] was evaluated following the same procedures as in Example 1, except that a cathode catalyst material formed by a method explained below was used. The results are shown in Table 1.

Please replace the paragraph at page 42, lines 2-7, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was formed and the cell performance were was evaluated following the same procedures as in Example 1, except that a cathode catalyst material formed by a method explained below was used. The results are shown in Table 1.

Please replace the paragraph beginning at page 42, line 8, through page 43, line 8, with the following rewritten paragraph:

Carbon particles carrying Pt particles were obtained by a coprecipitation method explained below. First, 20 g of carbon powders and 1,000 ml of water were used to form a suspension by using a homogenizer. This suspension was placed in a three-necked flask having a mechanical stirrer, reflux cooling pipe, and dropping funnel, and refluxed under stirring for 1 hr. Twenty minutes after 120 ml of an aqueous chloroplatinic acid (H₂PtC₁₆) (Pt = 42 mg/ml) were added, a solution prepared by dissolving 15.0 g of sodium hydrogencarbonate in 500 ml of water were was gradually dropped (the dropping time was about 60 min). After that, the resultant solution was refluxed for 2 hrs. The precipitate was transferred to a flask, refluxed over dilute sulfuric acid for 30 min, and filtered. The precipitate was well washed with pure water, transferred to a flask, and refluxed over pure water for 30 min. After being filtered, the precipitate was well washed with pure water. This precipitate was dried at 100°C. The dried precipitate was placed in a high-purity zirconia boat and reduced in a cylindrical oven at 200°C for 10 hrs by supplying 3% H₂/N₂ gas at a flow rate of 100 ml/min. After that, the temperature was returned to room temperature to obtain a catalyst precursor. Note that when taken out after being reduced, the catalyst was

cooled with dry ice and given non-combustibility by CO₂, thereby obtaining the catalyst precursor.

Please replace the paragraph at page 45, lines 7-12, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was formed and the cell performance were was evaluated following the same procedures as in Example 1, except that the thus obtained anode electrode and cathode electrode were used. The results are shown in Table 1.

Please replace the paragraph at page 45, lines 14-19, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was formed and the cell performance were was evaluated following the same procedures as in Example 1, except that an anode catalyst material prepared by a method explained below was used. The results are shown in Table 1.

Please replace the paragraph at page 47, lines 2-12, with the following rewritten paragraph:

Single cells of direct methanol polymer electrolyte fuel cells (DMFCs) were formed and the cell performance were was evaluated following the same procedures as in Example 1, except that carbon powders carrying anode catalyst particles having average diameters and compositions shown in Table 1 were used as anode catalyst materials, and carbon powders carrying cathode catalyst particles having average diameters and compositions shown in Table 1 were used as cathode catalyst materials. The results are shown in Table 1.

Please replace the paragraph at page 51, lines 3-16, with the following rewritten paragraph:

As shown in FIG. 2 described earlier, the slurry-coated carbon paper was placed between a pair of magnetic poles 6a and 6b, and the slurry was dried under a magnetic field of 1.2 tesla, thereby forming a cathode electrode having a catalyst carrying density of 1.5 mg/cm². The direction of the line of magnetic force was parallel to the thickness direction of the catalyst layer. When the obtained cathode electrode was observed with a TEM or FE-SEM, at least one part of the catalyst material particles were was arranged along a direction parallel to the thickness direction of the catalyst layer, i.e., at least one part of the catalyst material particles stacked along the thickness direction of the catalyst material.

Please replace the paragraph at page 53, lines 2-8, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was manufactured and the cell performance were was evaluated following the same procedures as in Example 10, except that the average diameter of PtFe particles of a cathode catalyst was changed to 2.0 nm as shown in Table 2. The results are shown in Table 2.

Please replace the paragraph at page 53, lines 10-17, with the following rewritten paragraph:

Single cells of direct methanol polymer electrolyte fuel cells (DMFCs) were manufactured and the cell performance were was evaluated following the same procedures as in Example 10, except that the composition, average diameter, and coercive force of each

cathode catalyst and the intensity of magnetic field were set as shown in Table 2. The results are shown in Table 2.

Please replace the paragraph at page 53, lines 20-24, with the following rewritten paragraph:

A cathode electrode was formed following the same procedures as in Example 10 except that carbon black particles carrying Pt particles having an average diameter of 2.5 nm [[was]] were used as a cathode catalyst material.

Please replace the paragraph beginning at page 54, line 16, through page 55, line 6, with the following rewritten paragraph:

As shown in FIG. 2 described earlier, the slurry-coated carbon paper was placed between a pair of magnetic poles 6a and 6b, and the slurry was dried under a magnetic field of 0.5 tesla, thereby forming an anode electrode having a catalyst carrying density of 3 mg/cm². The direction of the line of magnetic force was parallel to the thickness direction of the catalyst layer. When the obtained anode electrode was observed with a TEM or FE-SEM, at least one part of the catalyst material particles were was arranged along a direction parallel to the thickness direction of the catalyst layer, i.e., at least one part of the catalyst material particles stacked along the thickness direction of the catalyst layer. Also, the content of the catalyst material particles on that surface of the anode catalyst layer, which opposed a collector was larger than that of the catalyst material particles on the opposite surface.

Please replace the paragraph at page 55, lines 7-12, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was formed and the cell performance were was evaluated following the same procedures as in Example 10, except that the thus obtained cathode electrode and anode electrode were used. The results are shown in Table 2.

Please replace the paragraph at page 55, lines 14-21, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was manufactured and the cell performance were was evaluated following the same procedures as in Example 10, except that the composition, average diameter, and coercive force of the anode catalyst and the intensity of magnetic field were set as shown in Table 2. The results are shown in Table 2.

Please replace the paragraph beginning at page 55, line 23, through page 56, line 3, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was manufactured and the cell performance were was evaluated following the same procedures as in Example 10, except that an anode electrode similar to that explained in Example 10 and a cathode electrode similar to that explained in Example 20 were used. The results are shown in Table 2.

Please replace the paragraph at page 56, lines 5-11, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was manufactured and the cell performance were was evaluated following the same procedures as in Example 10, except that the intensity of the magnetic field in the magnetic field processing was changed as shown in Table 2. The results are shown in Table 2.

Please replace the paragraph at page 56, lines 13-19, with the following rewritten paragraph:

A single cell of a direct methanol polymer electrolyte fuel cell (DMFC) was manufactured and the cell performance were was evaluated following the same procedures as in Example 20, except that the intensity of the magnetic field in the magnetic field processing was changed as shown in Table 2. The results are shown in Table 2.